In situ observations on the crystallization of spodumene from aqueous solutions in a hydrothermal diamond-anvil cell

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Crystallization experiments were conducted in a new type of hydrothermal diamond-anvil cell (HDAC; type V) using $LiAlSi_2O_6$ (S) gel and H_2O (W) as starting materials. The sample chamber is a hole (0.1 mm diameter) at the center of a Re gasket (0.3 mm diameter and 0.25 mm thick), sealed by compressing the gasket with two parallel diamond anvil faces. A total of 21 experiments were performed at temperatures up to 950 °C and pressures up to 788 MPa. In the samples with relatively high S/W ratios, many small crystals formed in the melt phase during cooling. Those with low S/W ratios, only few crystals with smooth surfaces crystallized from the aqueous fluid in the presence of melt droplets, which were gradually consumed during the growth of the crystals, indicating rapid transfer of material from the melt to the crystals through the aqueous fluid. The nucleation of crystals started at 710 (±70) °C and 520 (±80) MPa, and crystal growth ended at 570 (±40) °C and 320 (±90) MPa, with the cooling *P-T* path within the stability field of spodumene + quartz in the S-W system. The observed linear crystal-growth rates in the aqueous phase, calculated by dividing the maximum length of a single crystal by the duration of the entire growth step [1, 2], were 4.7×10^{-6} and 5.7×10^{-6} cm/s for the cooling rates of 0.5 and 1°C/min, respectively.

Our results show that when crystals nucleate in the aqueous instead of the melt phase, there are fewer nuclei formed, and they grow much faster due to low viscosity of the aqueous fluid, which accelerates diffusion of components for the growth of crystals. Therefore, the large crystals in pegmatite most likely crystallized from aqueous fluids instead of hydrosilicate melt. This conclusion was further supported by our homogenization experiments in HDAC for crystal-rich inclusions in spodumene from Jiajika lithium pegmatite deposit in China. During heating, decrepitation of the fluid inclusions was prevented by applying external pressures (2.7 to 5.6 MPa) to the inclusions in the sample chamber of HDAC. In these inclusions, the H_2O-CO_2-NaCl fluid phase homogenized at ~290 ℃, followed by the melting of zabuyelite and other daughter minerals (i.e., quartz, calcite, spodumene, and unidentified minerals) during heating. Finally, the melt dissolved totally into the H_2O-CO_2-NaCl fluid, which represents the "boundary-layer liquid" [3, 4] from which the host spodumene crystallized. In other words, the spodumene crystals in the Jiajika pegmatite deposit crystallized from flux-rich aqueous fluids instead of hydrosilicate melt.

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On using natural chemical and isotopic tracers to monitor fracture surface area evolution in enhanced geothermal systems

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It has been proposed, and various trials are taking place, to inject fluids into geothermal systems to stimulate fracturing and hence increase fluid flow and heat-exchange efficiency in such enhanced geothermal systems (EGS). We are investigating a new approach to detect increases in fracture surface area in reponse to geothermal well stimulation using natural chemical and isotopic tracers. Our working hypothesis is that freshly-created fracture surfaces are out of chemical and isotopic equilibrium with newly flowing fluids, and thus subsequent mineral dissolution and precipitation generate transient chemical and isotopic signals that can be monitored in production wells. Such signals in turn could be interpreted through reactive transport modeling to infer induced changes and the temporal evolution of reservoir fracture reactive surface and permeability.

To test this hypothesis, a series of laboratory hydrothermal experiments were conducted using altered rhyolitic tuff from core taken at the Desert Peak geothermal field in Nevada, an EGS site. Two kinds of reactivity experiments were conducted at differing water-to-solid ratios: crushed tuff of variably sized fractions (600-710, 150-180 and 63-75 μm) and a solid rock wafer. These experiments were conducted in flexible Au bag autoclaves that allow multiple acquisitions of fluid/gas samples during experiments without perturbations of temperature and pressure conditions. Experiments were run from 15 to 60 days at 220˚C and 100 bars to maintain a single fluid phase. The initial fluid was high purity water, spiked with NaCl (0.1 M). Periodically during the experiments, fluid samples were drawn off and anlyzed for chemical and isotopic (e.g. $^{87}Sr/^{86}Sr$) composition. In batch experiments with 600-710 μm sized rock fragments, $^{87}Sr/^{86}Sr$ rose over the first several days then subsequently declined, followed by several reversals in trend over the next 6 days. Overall, $^{87}Sr/^{86}Sr$ roughly follows the Rb/Sr trend. In contrast, with the rock wafer experiment, after initially falling, $^{87}Sr/^{86}Sr$ increased along with Rb/Sr for sixty days. In the case of both experiments, the Sr concentration of the fluid fell or held steady despite changing $^{87}Sr/^{86}Sr$, suggesting the precipitation of Sr bearing phases concomitant with dissolution of primamy rock minerals (e.g., plagioclase, k-spar) and/or their alteration products (e.g., carbonates) with a range of $^{87}Sr/^{86}Sr$. A flow-through experiment with 600-710 μm material exhibited similar behavior. Simulations of the experiments using geochemical and reactive transport models are being conducted to investigate the types of reactions taking place and their dependence on solid-to-water ratios. Preliminary results indicate that plagioclase dissolution is accompanied by precipitation of Al hydroxides, zeolites/clays, secondary feldspars and calcite, yielding fluid composition trends that are sensitive to initial water/rock ratios.